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The Influence of Promoters
in Catalytic Combustion



THE INFLUENCE OF PROMOTERS
IN CATALYTIC COMBUSTION

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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THE HISTORY OF THE
CITY OF LONDON

FROM THE FOUNDATION
TO THE PRESENT

BY
J. H. P.

THE HISTORY OF THE
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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

.....Paul Alexander Anderson.....

ENTITLED.....The Influence of Promoters in Catalytic Combustion.....

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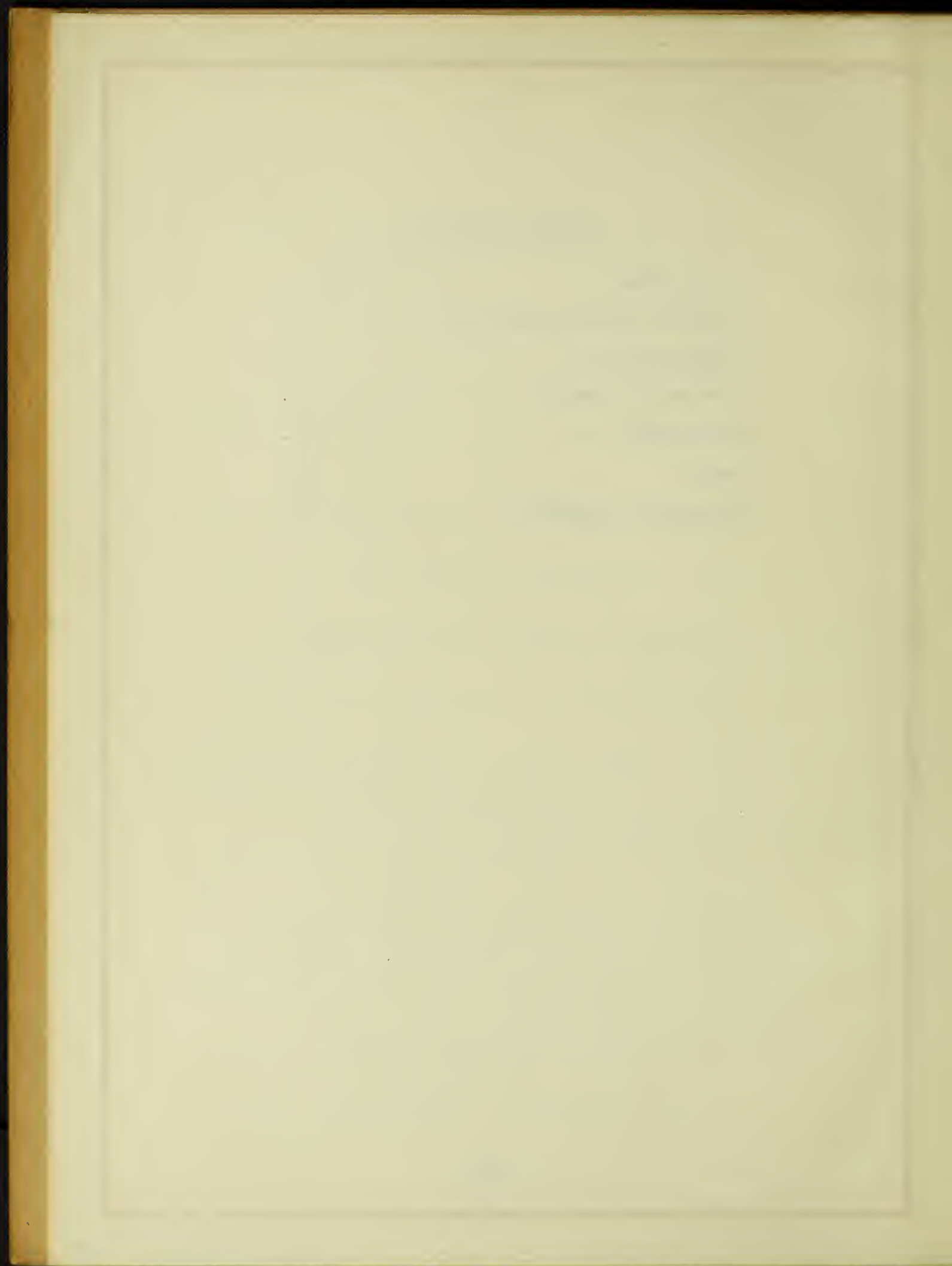
1871
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THE INFLUENCE OF PROMOTERS IN CATALYTIC COMBUSTION.

Introduction.

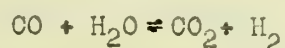
One of the major problems occupying the attention of the chemist today is the problem of catalysis. The theoretical chemist and industrial chemist are alike interested. The physical chemist is interested in developing a true and comprehensive theory of catalysis both for the intrinsic interest of the problem and for the light which its development will shed on the mechanism of chemical reaction in general. The industrial chemist is interested because a clear understanding of the laws underlying catalytic phenomena must lead to an enormous increase in the scope of the application to industrial manufacturing of processes essentially catalytic in character, processes already of great and ever increasing importance.

In investigating catalytic materials and catalytic phenomena in general minute quantities of foreign material mixed with the catalyst have been found to have an effect of enhancing the activating power of the catalyst far out of proportion to the amount of impurity present or to its individual catalytic activity in the reaction in question. This method of increasing the activity of catalysts has already received extensive technical application in the Haber process for synthetic ammonia, the Ostwald process for the oxidation of ammonia using non-platinum catalysts, the contact process for sulfuric acid manufacture, the manufacture of hydrogen from water gas, and in other processes. The nature of promoter action is at present unknown; several hypotheses have been advanced to account for promoter action in certain specific cases but a comprehensive theory has not as yet been proposed. There is thus presented one of the most interesting problems in the field of catalytic chemistry, the solution of which will go far to clear up the nature of catalytic action in general, just as the elucidation of the latter will supply a valuable point of attack upon the mechanism of all chemical reaction. It has been attempted in this investigation to

study the nature of promoter action as exhibited in the selective combustion of carbon monoxide in hydrogen.

Historical and Theoretical.

The work done up to the present time in investigating the nature of promoter action as exhibited in the selective combustion of carbon monoxide in hydrogen is very meagre. The study of the CO--CO₂ conversion was undertaken during the late war by the Munitions and Inventions Department in England and later continued by Dr. Lamb and his staff at Washington. In both instances the problem was approached on the assumption that the oxidation of carbon monoxide in a hydrogen-CO-oxygen mixture takes place indirectly, that is, that hydrogen is first oxidized to water at the surface of the catalyst whence the reaction proceeds in accordance with the well-known water gas equilibrium:



Hahn (Zeit.f.Phys.Chem., 44, 513 and 48, 735) subjected the water gas equilibrium to careful study at temperatures between 686°C. and 1400°C. He found that the Mass Action Law holds up to 1100 degrees and determined the following values for the equilibrium constant, K, in the expression:

$$K = \frac{(\text{CO})(\text{H}_2\text{O})}{(\text{CO}_2)(\text{H}_2)}$$

Temp. °C.	K (Obs)	K (Calc)
686	0.534	0.505
786	0.840	0.790
886	1.197	1.133
986	1.571	1.520
1005	1.65	1.597
1086	1.96	1.938
1205	2.126	2.457
1405	2.49	3.320

The calculated values for K are obtained by Luggin's formula:

$$\text{Log } K = \frac{-2232}{T} - 0.084631 \log T - .0002203 T + \text{const. (2.508)}$$

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If this formula be solved for a temperature of 500° (217°C) K is found to have the value 0.0200. Consider now, a gas mixture with the composition: $\text{CO} - 2\%$, $\text{H}_2 - 94\%$, and $\text{H}_2\text{O} - 4\%$ ($2\% \text{H}_2 + 2\% \text{O}_2$). In the equilibrium equation if x represents the concentration of carbon dioxide at equilibrium the equation becomes:

$$K = \frac{(2-x)(2+x)}{(94+x)(x)} = .2 \quad \text{whence } x = 1.2. \quad \text{The interpretation of this result}$$

leads to the conclusion that if the carbon monoxide-carbon dioxide conversion takes place according to the water gas reaction, the conversion of $2\% \text{CO}$ to $1.2\% \text{CO}_2$ plus $.8\% \text{CO}$ can take place only with the simultaneous formation of 4% water.

It follows that since the equilibrium constant increases in favor of the greater production of CO and water at higher temperatures and since the catalytic oxidation of carbon monoxide does not take place at temperatures far below 200°C that it should be impossible to effect a total conversion of carbon monoxide to dioxide in the presence of hydrogen without a correspondingly large production of water. Rideal (Jour.Chem. Soc. 115,993) however has been able to effect a total conversion of CO to CO_2 in the presence of hydrogen with a simultaneous formation of water far below that demanded by the water-gas equilibrium. The conclusion is that the formation of carbon dioxide and water is the result of two independent reactions: $\text{CO} + 1/2 \text{O}_2 \rightleftharpoons \text{CO}_2$ and $\text{H}_2 + 1/2 \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$

Rideal by determining the ratio of carbon monoxide to hydrogen burnt at different temperatures and with various catalysts has also shown that the relative rates of oxidation of carbon monoxide and hydrogen vary with the temperature and the catalytic material employed, that is, that various catalysts possess widely variant selective properties in promoting one or the other of the reactions, $\text{CO} \rightarrow \text{CO}_2$ and $\text{H}_2 \rightarrow \text{H}_2\text{O}$. This selective action was found to reach a maximum at low temperatures and to disappear entirely above 400° . Between 275 and 400° . the ratio of gases burned is determined - disregarding the selective action of the catalyst- by the value of the relative rates of desorption of the products of combustion, i.e. carbon dioxide and water, from the surface of the catalyst.

At temperatures above 400°C the ratio is determined merely by the ratio of partial pressures and follows the Law of Mass Action up to 1100° , as Hahn has shown, above which temperature the effect of dissociation becomes pronounced. Below 275°C carbon monoxide is preferentially adsorbed by certain catalysts, e.g. iron oxide and copper oxide, while the hydride forming catalysts such as palladium, platinum, and nickel, promote the oxidation of hydrogen even at low temperatures.

The study of the selective combustion of carbon monoxide in hydrogen has obviously served to bring out the specificity of action of various catalysts in a remarkable manner and it appeared probable that by carrying these investigations further through a study of the influence of small quantities of promoters on the unpromoted catalysts already studied, some light might be thrown on the nature of promoter action in general.

Experimental.

Apparatus: The apparatus employed consists essentially of a graduated gasometer, purifying and drying train, catalyst furnace, and duplicate absorptive trains. The gasometer was constructed of two gas bottles in the usual manner with connections for convenient filling and discharging at any desired rate. The purifying train consisted of two KOH bulbs in series and a drying tube charged with CaCl_2 and phosphorous pentoxide. The KOH bulbs serve the double purpose of removing any traces of carbon dioxide remaining in the gas mixture after the previous purification and of indicating the approximate flow rate of the gas being sent through the furnace. It was later found necessary to introduce a water-filled bulb between the drying tube and the catalyst furnace to furnish the trace of moisture found to be required for securing positive results with certain of the catalysts at low temperatures.

The catalyst furnace was of the type employed by Rideal (Catalysis in Theory and Practice) consisting of two concentric vertically fixed pyrex glass tubes, the outer wound with nichrome resistance wire, the inner containing the

catalytic material. The gas enters at the base of the outer tube and is heated as it passes up the annular space between the tube walls. It then passes down through the mass of catalytic material in which the thermometer is embedded and out through the absorptive train. The latter consists of a drying tube charged with phosphorous pentoxide and a KOH bulb filled with the usual 40% caustic solution. A very slight vacuum was applied at the termination of the absorptive train to equalize the pressure throughout the system and prevent diffusion of the gases through the rubber connections.

Preparation of Gases: The hydrogen was obtained variously from an electrolytic generator, ordinary Kipp generator, and cylinders, and was thoroughly purified in every case to remove traces of hydrogen sulfide and other impurities. Oxygen was obtained from cylinders or when this source was not available by heating a mixture of potassium chlorate and manganese dioxide; careful purification was also carried out in this case. The carbon monoxide was prepared by treating oxalic acid with concentrated sulfuric acid and removing the carbon dioxide formed by absorption with concentrated caustic solution. It was prepared in quantity and stored in gas bottles over caustic solution until used.

Preparation of Catalyst:

The copper catalyst was prepared by precipitating the hydroxide from a solution of the nitrate, boiling to obtain the black oxide, filtering and washing. The dry oxide was placed in clean, stoppered vials and reduced in the furnace just prior to use. In the preparation of the palladium promoted catalyst the palladium was added to the copper nitrate solution in the form of a measured volume of the solution of the nitrate of known concentration prior to precipitation of the hydroxide. The copper and palladium hydroxides are thus precipitated simultaneously and a uniform molecular distribution of palladium obtained. The quantity of sodium hydroxide used in precipitating this solution must be calculated since the basic salts of palladium are soluble in excess alkali. Just prior

to a series of determinations a small quantity of the dry oxide, which when placed in the stock bottle is in the form of thin cakes as removed from the filter, is broken into coarse grains approximately .1 cm. in diameter, placed in the inner tube of the catalyst furnace, and subjected to the alternate reducing and oxidizing action of hydrogen and oxygen (air) at progressively decreasing temperatures. The hydrogen and air used for this purpose were of course carefully purified before passed over the catalyst. The formation of water at 130°C was taken as an indication that the catalyst was sufficiently active for use.

Determination of the $\text{CO}:\text{H}_2$ Ratio-General Considerations:

As Rideal has found in his work on the selective combustion of carbon monoxide in hydrogen, it is impossible to obtain accurate or significant results in terms of absolute quantities of carbon monoxide and hydrogen oxidized due to appreciable fluctuations in the activity of the catalyst during even short series of runs; the ratio of the rates of combustion of the CO and hydrogen may however be expected to remain fairly constant under given conditions of temperature, gas composition etc. and have in fact been shown to be capable of quite accurate determination.

Approximately 4cc of catalyst was used in each determination and a gas mixture of the composition: hydrogen 80%, carbon monoxide 10%, and oxygen 10%, employed throughout. Approximately 500 cc. of gas were passed over the catalyst for each determination, the rate of passage being varied to give an approximately equivalent conversion of the constituents at all temperatures, that is, to maintain the oxygen concentration constant and thus eliminate the variable which might otherwise enter. It is important to note that the gas must be passed at such a rate as to preclude the formation of a "dead" layer of reactants on the surface of the catalyst; in the presence of such a layer the reaction of fresh constituents takes place only after their diffusion through this layer to the catalyst surface, whence their relative rates of reaction become dependent on

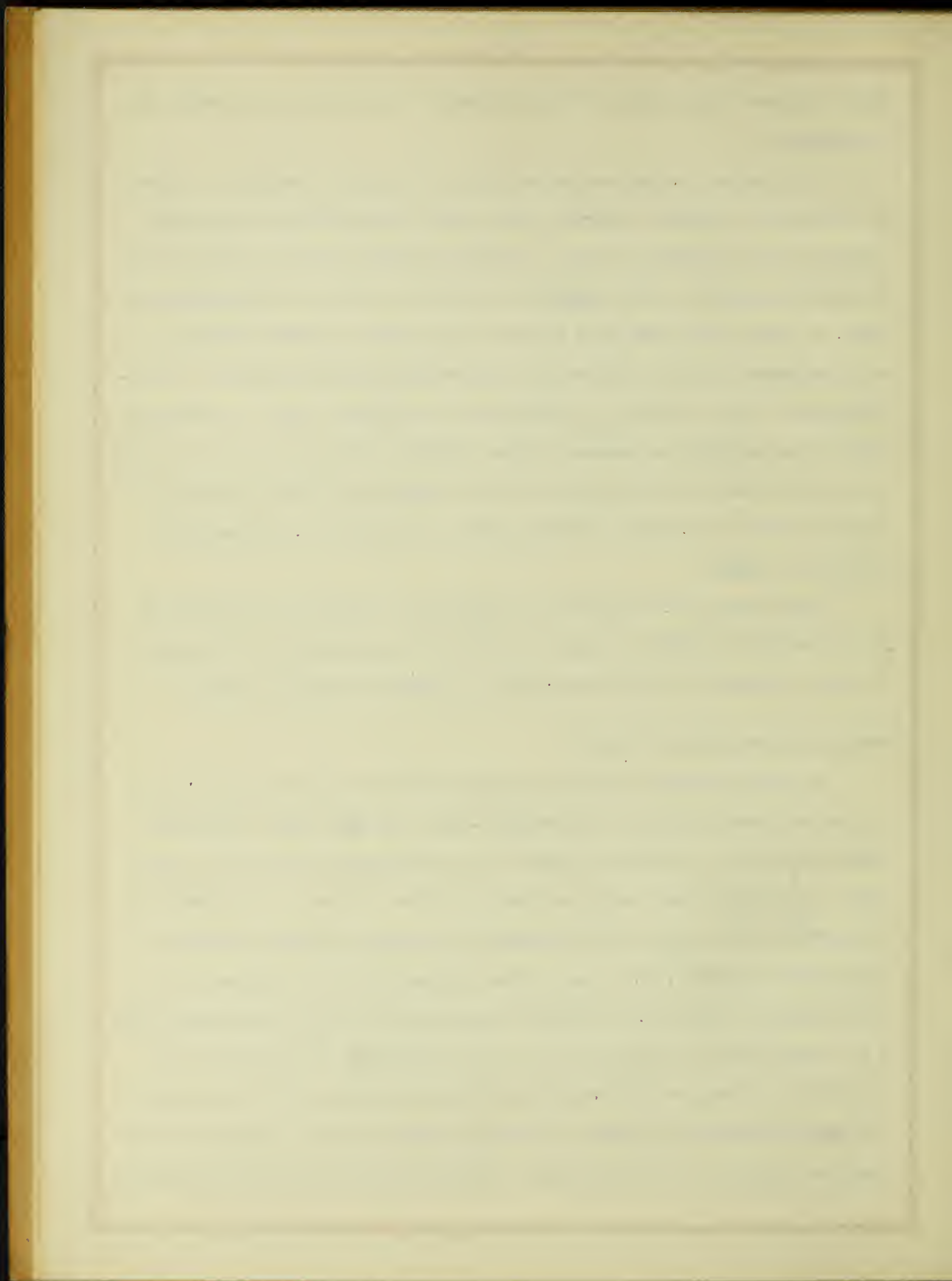
their diffusion rates rather than their selective adsorption on the surface of the catalyst.

In selecting a catalyst-promoter system it appeared desirable to select as a foundation catalyst a material which should preferentially adsorb carbon monoxide at low temperatures and as a promoter a material with a strongly marked specific catalytic action opposite in effect to that of the foundation catalyst. By such a choice the exact action of the promoter- whether additive or peculiar-becomes clearly differentiated and consequently easily studied. The requirements of such a system are admirably met by employing copper as foundation catalyst and palladium as promoter. Copper exhibits a marked preferential adsorptive action on carbon monoxide (at low temperatures) while palladium is the most active of the hydride forming group in activating the combination of hydrogen and oxygen.

Five series of determinations at temperature intervals of approximately 20° between 260° and 160° were made with each of three catalysts, pure copper, (2) copper promoted by 1.0% palladium, and (3) copper promoted by .1% Pd.

Results with Pure Copper Catalyst:

The results obtained with pure copper catalyst served to verify the form of curve previously obtained by Rideal (Jour. Chem. Soc. 115, 993). Plotting the ratio $\text{CO}:\text{H}_2$ burned as ordinates against the corresponding temperatures as abscissae a practically linear curve was obtained between the ratio 9:1 at 160° and 1:2 at 260°C . Great difficulty was encountered in securing reliable results at temperatures below 200° . The action of the catalyst below this temperature was very erratic and often nil. In several instances after giving a considerable yield of carbon dioxide and water for one or two determinations it suddenly lost its activity entirely as if attacked by an energetic poison. It was later found that the introduction of a trace of water vapor often served to increase and prolong the activity of the catalyst mass. A KOH bulb filled with water was accord-



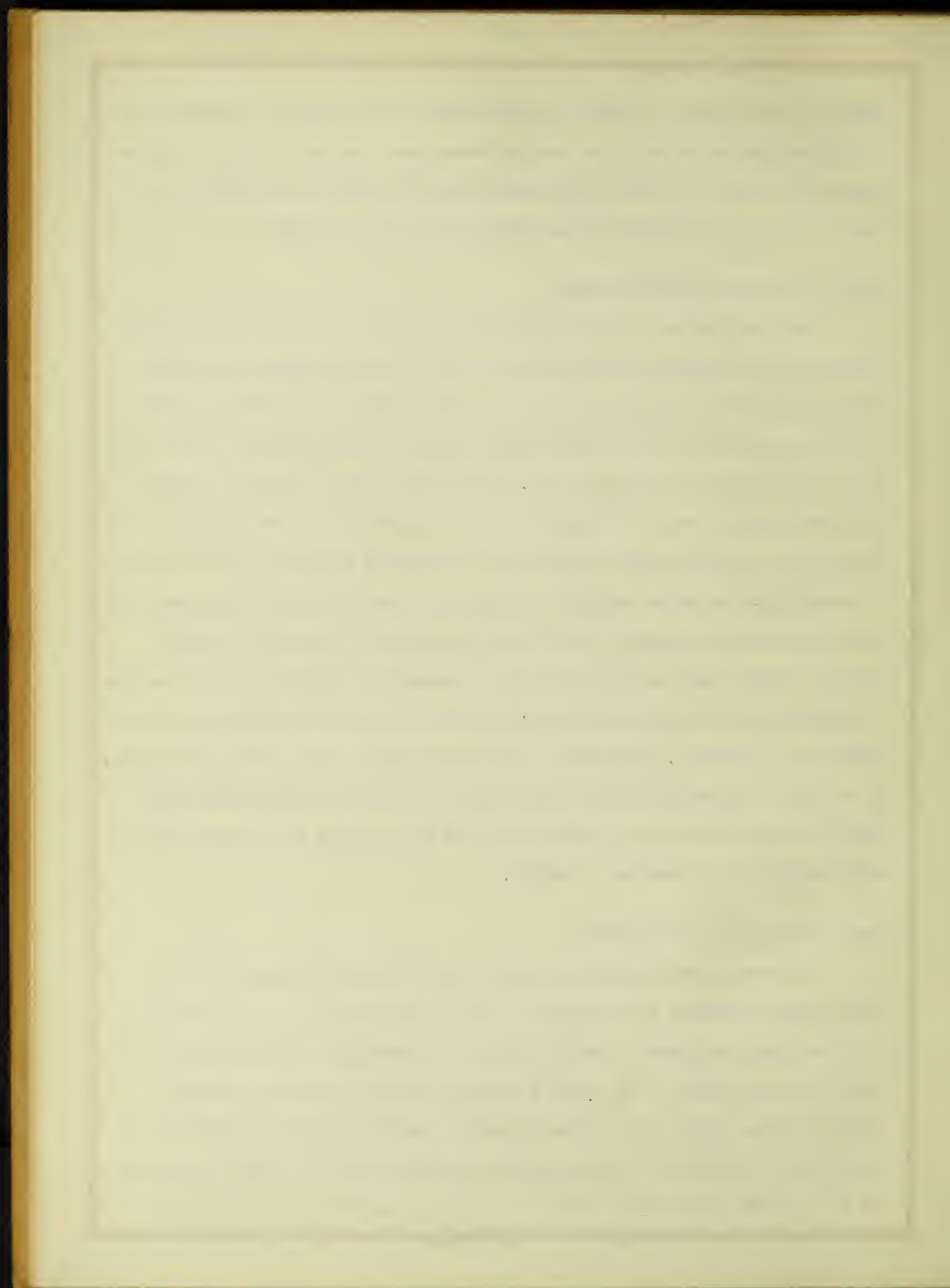
ingly introduced into the purifying train between the drying tube and the furnace and weighed before and after each determination. The loss in weight, representing the weight of water vapor carried into the furnace was subtracted from the weight of water absorbed on the opposite side of the furnace.

Copper promoted by 1.0% Palladium:

The determination of the ratio values with this catalyst was attended by little of the difficulty encountered with the use of pure copper. The results obtained in practically every run were positive, while a considerably greater fractional conversion of both constituents (CO and H_2) was obtained in each case for a given temperature and flow rate. The promoted copper appeared to be much more consistent as well as energetic in its action and to possess a greater durability than the unpromoted catalyst. The curve obtained by plotting ratios against temperatures as before exhibits a well defined maximal at 175°C . The ratio of carbon monoxide to hydrogen burned at each temperature interval from 260° to 175° was greater than that given for the corresponding temperature by the unpromoted copper, indicating as will be later pointed out that the action of the palladium is not additive, while below 175° the ratio was found to fall off sharply. In the small temperature interval between 175° and 160° the ratio $\text{CO}:\text{H}_2$ burned falls from 12:1 to 5.5:1. The reasons for this abrupt break in the curve will be considered in the discussion of results.

Copper Promoted by .1% Palladium:

The results obtained with the use of copper catalyst promoted by one-tenth percent palladium were unexpected and of considerable interest. This catalyst was found to produce a greater relative conversion of carbon monoxide than either the pure copper or one percent palladium "alloy" previously tested; the ratio of carbon monoxide to hydrogen burned appreciably exceeded that for either of the other catalysts at every temperature interval over the entire range between 175° and 260° and exceeded that for the one percent alloy over the entire



range investigated. A maximum conversion ratio of 13.5:1 was obtained at 175° as against 12:1 for the copper promoted by one percent palladium. A larger number of non-checks was obtained than in the series of determinations with the one-percent alloy and fewer than in the determinations with pure copper catalyst. Considerable difficulty was experienced as with copper in securing uniform results at low temperatures. With respect to its durability and resistance to poisons this catalyst appeared to be superior to pure copper catalyst and considerably inferior to the copper promoted with one percent palladium.

Graph:

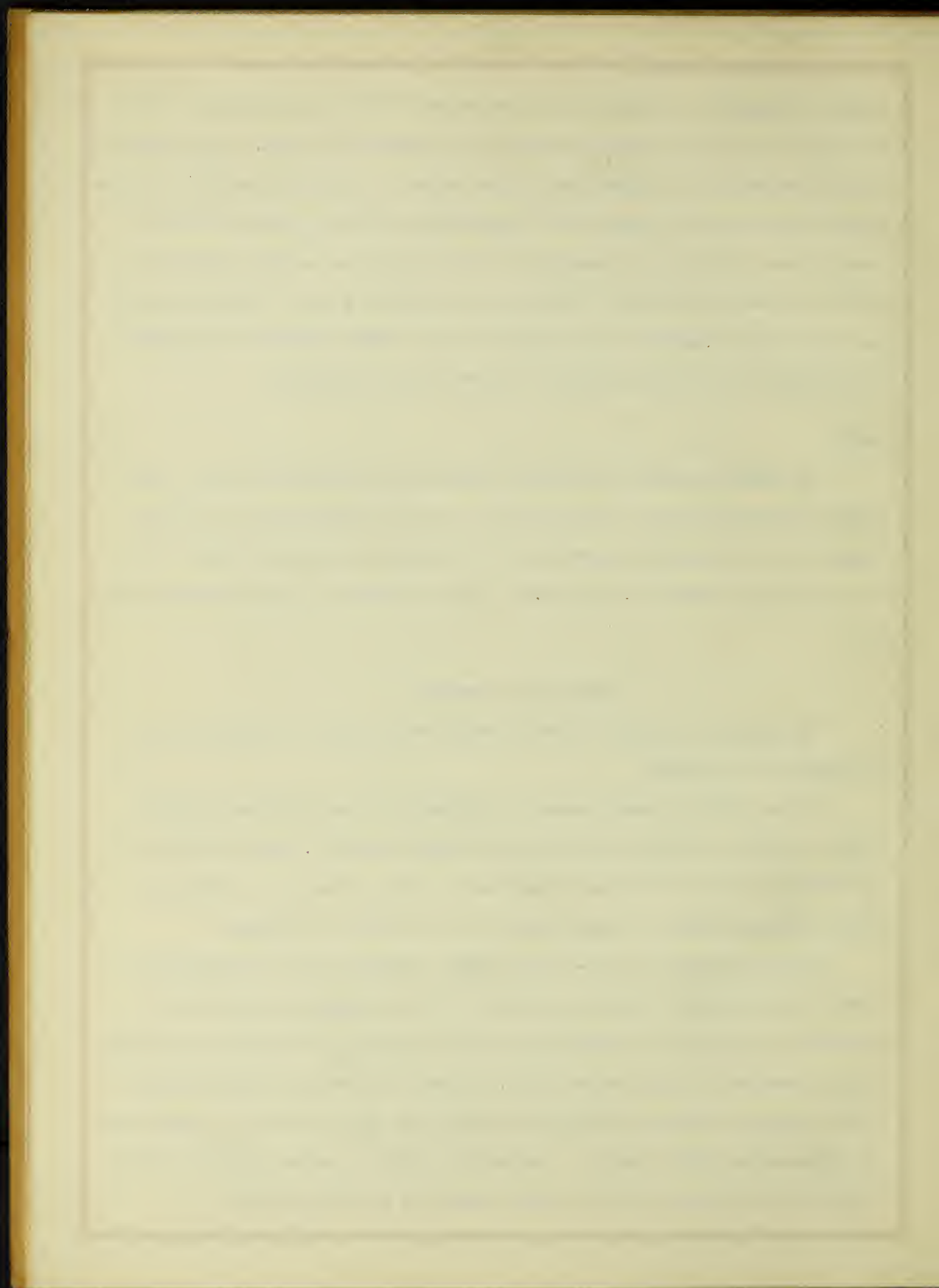
As already mentioned a graph was constructed plotting the values of the carbon monoxide-hydrogen ratios obtained at various temperatures as ordinates against the corresponding temperatures as abscissae. The interpretation of the curves and the results which they depict will be taken up in the following section.

Discussion of Results.

The points of peculiar interest brought out in this investigation may be enumerated as follows:

(1) The effect of small amounts of palladium in increasing the ratio of carbon monoxide to hydrogen burned over the copper catalyst. Were the effect of the palladium additive it would be expected to decrease this ratio since as a hydride-forming catalyst it should promote the oxidation of hydrogen.

(2) The occurrence of well-defined maximal points in the ratio-temperature curves of the promoted catalysts. The ratio of CO to hydrogen burned in each case falls off sharply at temperatures slightly higher and lower than the temperature represented by this maximal point. The curve for the pure copper catalyst on the contrary exhibits no maximal and crosses the other curves at a temperature of approximately 165° . Thus at a temperature of 160° a greater selective activation of CO is obtained with pure copper than with promoted catalyst.



(3) The apparent anomaly presented by the fact that copper promoted by one-tenth percent palladium gave higher ratios for carbon monoxide to hydrogen burned than those given by the catalyst promoted by one percent Pd, which itself gave higher ratios than those obtained with pure copper.

The promotive, i.e. non-additive, effect of the palladium and the decrease of this effect with increasing concentration of promoter may be explained on the basis of a theory proposed by Bancroft (Jour. Phys. Chem. 20, 85) and further developed by Rideal (Journ. Amer. Chem. Soc. 42, 749). Bancroft proposed the hypothesis that the protective action displayed by certain colloids in stabilizing certain other hydrosols, e.g. colloidal platinum, was due to the peptizing action of the protective colloid. Rideal seeking to expand this theory with the view to throwing some light on the nature of promoter action in catalysis, investigated the mutual effect of platinum and palladium when reduced together and employed as hydrogenation catalysts. He found that the admixture of a small quantity of either constituent greatly increased the activity as well as the stability of the other constituent when used alone. A mixed sol containing the constituents in the proportion of Pt 9.8 mg. and Pd .2 mg. was found to be fully as active as pure palladium. "This suggests the hypothesis that promoters may in part function as peptizing agents for colloidal catalysts or for catalysts which pass through a colloidal stage at some stage in their preparation."

In the light of this theory the role of the palladium promoter in the present investigation becomes clear. At the time of the simultaneous precipitation of the basic salts of copper and palladium from the solution of their nitrates, it may be easily conceived that the palladium salt in the sol condition acts as an active peptizing agent for the copper sol, thereby increasing its state of division and subsequent catalytic activity. The palladium in this case, unlike that in the Pd-Pt combination investigated by Rideal, has a specific catalytic action opposite to that of the catalyst which it promotes. As its concentration in the copper catalyst increases, therefore, its effect is to progres-

sively decrease the ratio of carbon monoxide to hydrogen burned by increasing the rate of oxidation of hydrogen. The cause of the increase in the total fractional conversion observed also becomes clear. It would appear then that the maximum promotive effect of palladium on copper would be obtained by determining the concentration of palladium for which the peptization effect would be as complete as possible while the specific catalytic action of the palladium approached as near a minimum as possible, that is by balancing the effects.

The occurrence of the maximal points in the curves for the promoted catalysts may be explained by the fact that as the temperature decreases beyond a certain minimum the selective activation of carbon monoxide by copper suddenly falls off while palladium continues to have a powerful activating influence on hydrogen.

In conclusion some of the possibilities for further work in the direction of this investigation may be pointed out. It would be desirable for example to secure data similar to that obtained for the three catalysts tested in the course of this research, for copper promoted by palladium in concentrations intermediate between .1% and 1.0% and in concentrations above and below this range. The determination of the concentration at which the curves for pure copper and promoted catalyst coincide, that is, the concentration at which the peptizing and specific catalytic effects of the palladium are equal, should be of interest. The curve for pure palladium should be determined for reference purposes. Finally the investigation of other combinations of catalyst and promoter in connection with the same or other reactions would inevitably be of great value in corroborating or modifying this theory and formulating a generalized theory for the nature of promoter action.

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1853

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Ratio
CO:H₂

Graphical Representation of
Ratios CO:H₂ burned with var-
ious catalysts at various temp-
eratures.

14:1

13:1

12:1

11:1

10:1

9:1

8:1

7:1

6:1

5:1

4:1

3:1

2:1

1:1

1:2

1:3

1:4

Pd 0.1 Percent

Pd 1.0 Percent

Pure Copper.

160

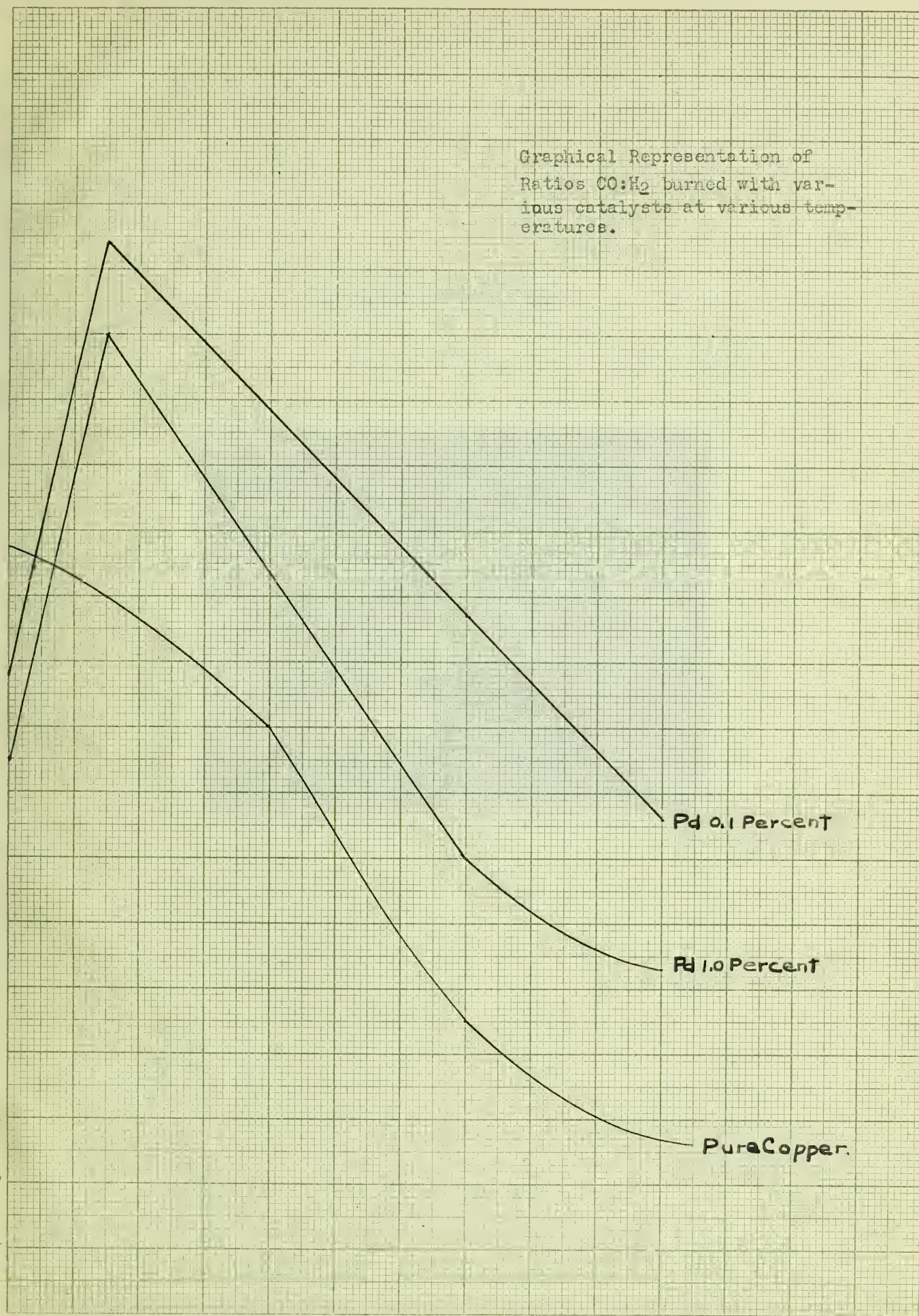
180

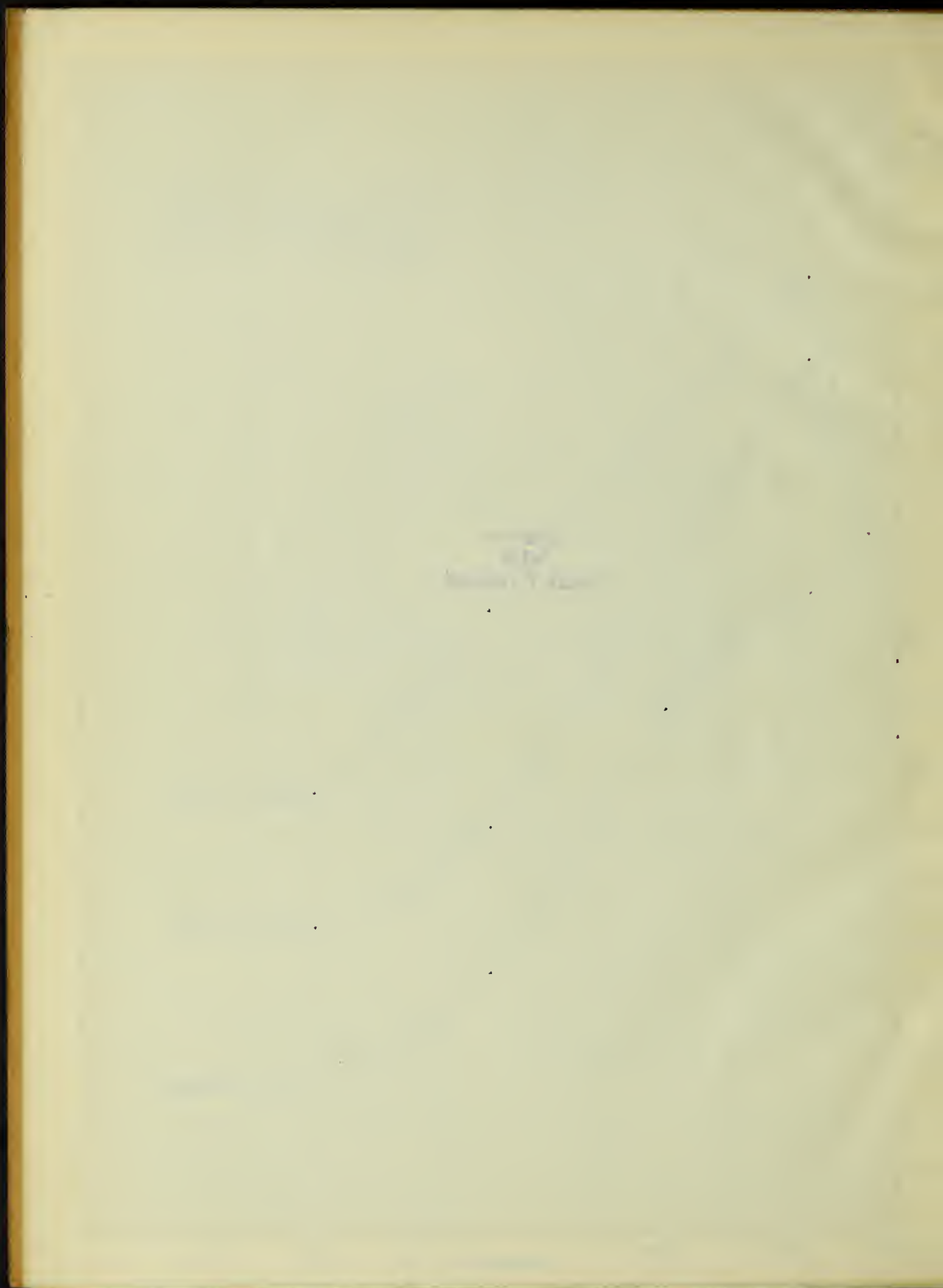
200

Temperature °C

260

280





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